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MICROSCOPIC CONTROL OF METALLIZATION STABILITY

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ABSTRACT

Metallization stability on semiconductor surfaces depends on atomic interdiffusion at two interfaces, namely the semiconductor metal junction and the overlayer atmosphere interface. Recent progress in controlling the stability of these interfaces derived from the use of powerful nondestructive analytical tools of local interface composition. We summarize here synchrotron radiation photoemission studies of metallic overlayers on Si(lll) and GaAs(ll0) surfaces. We focus on the use of diffusion barriers to control atomic interdiffusion, and on the effect of oxidizing atmospheres on metal and semiconductor composition.

INTRODUCTION

Corrosion and electromigration are two critical phenomena that limit long-term reliability of metallization patterns in integrated circuits. The formation of passivating layers to protect the metal from oxidizing environments, and the use of diffusion harriers in the interface region are two methods that offer promise of controlling corrosion and electromigration without imposing a radical change in materials or in fabrication technology. Both methods modify the local environment of one of the two interfaces present in the system, i.e. the overlayer-atmosphere interface and the semiconductor-overlayer interface. In fact, the two interfaces are thermodynamically coupled and the modification of one of the two may result in modification of the other. Recent studies of $\mathrm{Au}_*^{-1/2}~\mathrm{Ag}^3$ and Cr^5 overlayers on Si(111), for example, have shown that exposure to oxygen yields growth of a Si-oxide layer on top of the metal, and that such a process is strongly dependent on the morphology of the silicon-metal interface. For different metals, such as Sm and Cs,6,7 the oxide is nucleated at the metalsemiconductor boundary, i.e. below the metallization. These two aspects of enhanced oxidation in the presence of a metal overlayer could be exploited in different ways. When the oxide is nucleated on top, it may represent a good passivating layer to prevent corrosion of the metallization. When the oxide is nucleated underneath

the metal, ultrathin metal overlayers can be used as catalysts of semiconductor oxidation and allow low-temperature oxide growth. After growth of an oxide of suitable thickness, the metal catalyst can be removed with a number of etching techniques. 8

Atomic interdiffusion at semiconductor-metal interfaces takes place during function formation and processing for a large number of metals, 9,10 even when no electric field is applied. Interdiffusion has been observed even at liquid nitrogen temperature, 11 it may be chemically activated, 11 and it determines the microscopic junction profile and the stoichiometry of the interface reaction products. For compound semiconductors, the preferential diffusion of one of the semiconductor constituents through the interface may affect the dominant type of electrically active defects that remain near the semiconductor surface. Such defects, together with new localized interface states 10 produced by the local reaction of metal and semiconductor atoms, determine the Schottky barrier and the transport properties of the junction. To interpose suitable interlayers between the semiconductor and the metal has therefore the potential to control the junction profile and modify the Schottky harrier. 12,13

In this paper we summarize recent studies of these phenomena with local surface probes for well characterized, atomically clean Si and GaAs surfaces. We are still far away from practical

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Metallization stability on semiconductor surfaces depends on atomic interdiffusion acrosss the semiconductor/metal junction and at the overlayer/ atmosphere interface. We summarize here studies of metallization stability on Si and GaAs surfaces. We focus on the use of diffusion barriers to control atomic interdiffusion, and on the effect of oxidizing atmospheres on metal and semiconductor composition.

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application of matal passivation, catalytic oxidation and ultrathin diffusion harriers in device fabrication on technological—grade semiconductor surfaces. However, a practical exploitation of these phenomena requires a basic understanding of the microscopic mechanisms involved, and this is the major goal of our effort.

EXPERIMENTAL NOTES

Synchrotron radiation emitted by charged particles circulating in a storage ring exhibits a continuum spectrum extending from the infrared to the X-ray region and is linearly polarized in the plane of the orbit. In a typical photoemission experiment a monochromatic synchrotron radiation beam impinges on the sample surface at the focus of an electron energy analyzer. Angle integrated photoelectron energy distribution curves (EDC's) provide information on the energy distribution of the electron states below the Fermi level. In an ideal one-electron picture the EDC's reproduce the initial electron DOS distorted by the matrix element of the optical excitation and superimposed on a smooth secondary background due to inelastically scattered electrons. 9,10

The use of synchrotron radiation allows one to tune the photon energy and exploit the different energy-dependence of the photoexcitation probability of electron states with different elemental and orbital character. Also, the sampling depth of the technique depends on the energy-dependent photoelectron escape depth. Therefore, by varying the photon energy while monitoring the characteristic emission from one of the elements present at the surface, one can vary the sampling depth and obtain a nondestructive depth-profile of interface composition.

Most experiments described here were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Radiation from the 240 MeV or the 1 GeV electron storage rings were monochromatized by a "grasshopper" grazing incidence monochromator and focused inside our photoelectron spectrometer (operating pressure $< 5 \times 10^{-11}$ torr). Si(111) 2x1 and GaAs(110) 1x1 surfaces were obtained by cleavage in situ, and metal overlayers were deposited from resistively heated evaporators at pressure $< 2 \times 10^{-10}$ torr. with overlayer thickness measured by a quartz thickness monitor. Exposure to oxygen was performed in the 10^{-7} - 10^{-3} torr range with pressure monitored by a low-emission ion gauge. For conparison we also conducted oxygen chemisorption studies on free St(111) and GaAs(110) surfaces under the same conditions. Catalytic oxidation promotion effects are measured by comparison with the results for the free surface.

Photoelectrons were collected and analyzed in angle-integrated EDC's with a commercial hemispherical analyzer, with overall resolution (electrons + photons) of 0.25-0.40 eV. EDC's for the emission from elemental core levels are shown after subtraction of a smooth secondary background. The intensity of a core level provides information on the spatial concentration of the

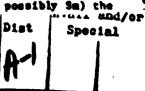
corresponding element. The binding energy of the core level, together with the characteristic valence band emission, were used to gain information on the chemical reactions taking place at the interface and on the character of the reaction products.

RESULTS AND DISCUSSION

OXIDATION STUDIES - The deposition of most (but not all) metal overlayers on Si and GaAs surfaces yields an increase of the oxygen uptake rate relative to the clean semiconductor surface. Metals as diverse as Au. 1-3 Ag. 1-3 Cu. Pd. Cr. Cs. Na, and Su have all been shown to give rise to such an effect. In Fig. 1 we show the effect of oxygen exposure on the Si 2p core lineshape for a numer of ultrathin metal overlayers (monolayer (ML) range). Spectra for Sa (1.5 ML), Cs (1 ML), Na (1.5 ML) and Cr (2 ML) overlayers on Si(111) are shown before (dashed line) and after (solid line) exposure to 100 L of oxygen (24 L for Cs). For comparison we also show (bottom-most spectrum) results for the oxidation of the free Si(111) surface. The overlayers included in Fig. 1 are those which exhibit the largest oxygen uptake rate. We have chosen comparable metal coverages for all overlayers. Higher metal coverages yield similar or higher oxygen uptake rates. The vertical hars in Fig. 1 at 0.9, 1.8, 2.6 and 3.5 eV mark the position of the chemically shifted Si 2p contribution observed by Hollinger and Himpsel14 during Si(111) oxidation and associated by these authors with Si atoms bonded to 1, 2, 3 and 4 oxygen atoms, respectively. Figure 1 shows that the reaction products involve nonequivalent oxidation states for silicon, and are consistent with what could be expected for a disordered, substoichiometric 5102 phase. In the case of Cr, as well as Au, 1-3Ag 3 and possibly the other transition metal examined, 4 the Si oxide appears to nucleate on top of the metal overlayer. A similar situation is encountered during oxidation of transition metal stlicide layers on silicon. 15,16 Most models proposed to explain this effect suggest that the formation of a silicide-like interface reaction product breaks up the sp3 configuration of the Si substrate so that the Si atoms at the interface would be in a metallic environment with "disrupted bonds" and they could easily be oxidized. Abhati et al. and, more recently, d'Heurle et al. 16 propose that a self-sustaining mechanism exists for which a flow of Si atoms is established through a silicon-metal silicide-like layer located between the growing oxide and the Si substrate. This layer would make Si atoms with broken sp³ configuration and "weaker" Si-Si bonds available for oxidation. The incoming oxygen would then react preferentially with \$1 and displace the metal from \$1 so that the metal would become available for intermixing with the substrate and produce further silicide.

This model does not seem to apply in full to the low-electronegativity overlayers Sm, 6 Cs, 7 and Na. 7 For Cs and Na (and possibly Sm) the





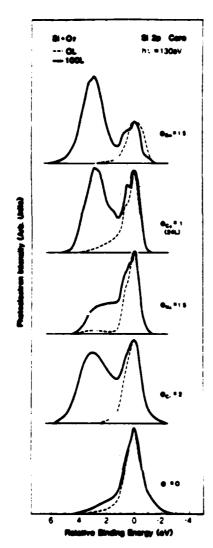


Fig. 1 — Si 2p core emission before (dashed line) and after (solid line) exposure to 190 L (24 L for Cs) of oxygen. We show results for the free Si surface (bottom-most EDC) while spectra displaced upward show the effect of Cr, Na, Cs, and Sm overlayers on Si oxidation. The vertical bars mark the position of Si 2p oxide features associated by Hollinger and Himpsel (Ref. 14) with Si atoms coordinated with one, two, three, and four oxygen atoms.

Si-oxide appears to nucleate below the metallic layer. Furthermore, the alkali metals do not intermix with silicon, do not form silicide-like reaction products, and they do not break the sp³ hybridization of the Si surface atoms.

We have proposed that for low-electronegativity overlayers the establishment of a large surface dipole is responsible for oxidation promotion. The chemisorption of low-electronegativity metals induces a modification of the electrostatic potential in the surface region. The metal valence electrons are polarized toward the substrate surface leading to a dipole layer which raises the electron levels of the surface

relative to the vacuum level. The rigid shift of the Fermi level yields a measurable reduction of the work function. If a molecular species is adsorbed within the surface dipole layer, the energy shift of the molecular level is less pronounced than that of the substrate levels. This may result in charge transfer to molecular antibonding orbitals, and formation of atomic oxygen that can react with Si atoms in the interface region.

Similar phenomena, i.e. the nucleation of semiconfuctor oxides on top or below a metallic overlayer, have been observed on GaAs surfaces. Without a metallic overlayer the GaAs(110) surface is relatively unreactive upon oxygen exposure. At room temperature and at low oxygen pressure only submonolayer oxygen coverages are obtained. Metallic overlayers including Cr, Au, 5 Sm, 6 and Na¹⁷ have been shown to yield increase of the oxygen uptake rate, and the formation of Ga and As oxides. Most metals intermix with GaAs upon deposition giving rise to arsenide-like interface phases and/or metal-Ga alloys. The similarity in the chemical bonding of silicide and arsenide phases inspired the sugquestion that a self-sustaining oxidation mechanism similar to the one proposed by Abbati et al. might be active also for transition metals on GaAs. The supporting evidence, though, is still scarce. It is true, for example, that Ag overlayers on GaAs do not give rise to oxidation promotion effects, and, correspondingly, most authors have indicated that the GaAs-Ag interface shows little or no atomic interdiffusion and no arsenide formation. However, it is often still unclear (Cr) if the oxides are nucleated on top or below the metallization layers, and the nature of the oxide species is also not completely clear. In Fig. 2 we show the situation for Sm overlayers on GaAs. The As 3d emission is shown normalized to the main emission feature after subtraction of the secondary background. The zero of the hinding energy scale corresponds to the initial core binding energy for the clean surface in flat-band conditions. The hottom-most EDC is representative of the coverage range where divalent Sm species dominate. The other EDC is representative of the coverage range where trivalent Sm species dominate. The spectra are shown before (dashed line) and after (solid line) exposure to 1000 L of oxygen. Oxygen exposure gives rise to two well-defined oxidized features: a broad line near the zero of the energy scale, and a high binding energy feature near 3 eV. Vertical bars 1-4 in Fig. 2 indicate the position of As 3d feature observed by Landgren et al. 0.8, 2.3, 3.2 and 4.2 eV below the initial substrate As 3d binding energy, and associated by these authors with As atoms coordinated with one, two, three and four oxygen atoms, respectively. Vertical bar 5 corresponds to the position of the As 3d core level observed in As 203 by Su et al. 19 To results of Fig. 2 indicate the formation of two main oxide phases: an As oxide where low oxidetion states are present, and a second high stahility phase similar to As203.

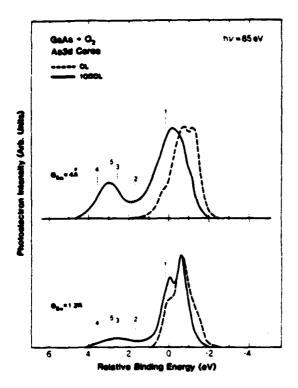


Fig. 2 - As 3d core emission at hv = 85 eV from GaAs(110) surfaces before (dashed line) and after exposure to 1000 L of oxygen. Before oxidation the result of As interaction with mostly trivalent Sm atoms is the emergence of a low binding energy 3d contribution at about -1.2 eV associated with the formation of arsenide-like interface species. The zero of the binding energy scale corresponds to the initial flat hand As 3d hinding energy for the free surface. In this exposure range oxidation of the free surface yields only minor modifications of the core lineshape while the presence of Sm overlayers yields oxidation promotion effects. Oxidation gives rise to two distinct oxidized As features, one centered at about 3 eV, and a second one near the zero of the hinding energy scale that involves lower oxidation states. The vertical bars 1-4 mark the position of the oxidized As 3d features observed by Langren et al. (Ref. 18) for As coordinated with one to four oxygen atoms. The vertical bar 5 marks the position of the As 3d core level in As₂0₃, from Su <u>et al</u>. (Ref. 19).

DIFFUSION BARRIER STUDIES — Very few studies exist of the microscopic mechanism that determines the properties of diffusion barriers. All interlayers at GaAs(110)-metal interfaces have been shown to change dramatically atomic interdiffusion through the interface. ²⁰ All interlayers at the CdS-Au interface have also been shown to change the Schottky barrier. ¹² With increasing interlayer thickness the macroscopic junction behavior evolves from rectifying to ohmic. The mechanics underlying this impressive result is still subject of debate. On Si, Cr interlayers at the Si(111)-Au interface exhibit a striking

nonmonotonic effect. 21 A critical interlayer thickness of about 9A is necessary at room temperature to observe a "diffusion harrier" effect. Between 2 and 9A the interlayer actually promotes the Si-Au intermixing. For coverage less than 2A, the interlayer has a slightly negative effect on interdiffusion. This strikingly nonmonotonic hehavior is related to the existence of three different stages of Si-Cr reaction, corresponding each to a different morphology of the interface region, a different microscopic arrangement of the Si atoms and, hence, a different energy content of the Si-Si bond. 13 Promotion of Si-Au atomic interdiffusion is related to an increase in reactivity of the Si surface atoms in the coverage range where a Si-Cr silicide-like interface phase is formed. When Cr and Si react the average Si-Si binding energy is reduced and the broken surface bonds represent sites where the chemically driven Si-Au intermixing may start. In the absence of an applied field the chemically activated character of the interdiffusion is emphasized by the sharp reduction in intermixing that occurs for interlayer thickness above 9A. In this coverage range unreacted Cr is present on top of the Si-Cr silicide and acts as an effective diffusion harrier for intermixing.21

In those cases in which the driving force for interdiffusion is not simply chemical, such as during high temperature processing or electromigration, the diffusion barrier may still be effective on the basis of two possible microscopic mechanisms. Chemical trapping of the moving species in the interface region may be possible by choosing an interlayer with large chemical affinity for the diffusing atoms. The ensuing chemical reaction could produce interface reaction products that structurally or electronically block the microscopic avenues for entropic and chemically activated diffusion.

Alternatively, the establishment of an electrostatic dipole field at the semiconductor-metal interface may prevent diffusion of polar species without the formation of new reaction products.

One can distinguish between these two mechanisms on the basis of microscopic analysis of the interface region (depth profiling) or from the dependence of the diffusion barrier effect on interlayer thickness. In Fig. 3 we show for example the case of Al interlayers at the GaAs(110)-Or interface. In the top section of the figure we describe schematically the geometry of the interface region. The Al interlayer acts as a marker of the interface, but also strongly modifies atomic interdiffusion. This can be seen in the bottom-most section of Fig. 3 where the apparent Ga/As ratio, obtained from the integrated emission intensity of the Ga 3d and As 3d core levels is shown as a function of interlayer thickness at a constant Cr coverage of 10A. Taking as unity the value of the ratio when no interlayer is present, one sees an almost 100% increase in the ratio when a thin (1A) Al interlayer is interposed between GaAs and Cr. Plots of the As and Ga 3d emission in the same section of Fig. 3 show that the trend towards a Ga-rich

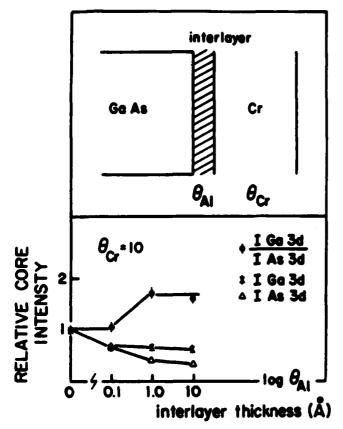


Fig. 3 — Top: Al interlayers at the GaAs-Cr interface act as a diffusion barrier and control atomic interdiffusion through the interface. Bottom: The Ga/As ratio from the integrated intensity of the Ga 3d and As 3d core emission is plotted as a function of Al interlayer thickness at a constant Cr coverage of 10A. Shown also for comparison are the As 3d and Ga 3d core intensities. All values are normalized to the emission intensity observed when no interlayer is present.

outdiffusion is maximum already at 1Å of interlayer thickness and remains relatively constant at higher interlayer thickness. This is in sharp contrast with the case of Al interlayers at the GaAs-Au interface, ²⁰ for which an increase of over one order of magnitude was observed in the relative Ga to As outdiffusion, but the effect was shown to increase monotonically with interlayer thickness. We proposed ²² that in the Cr case the dipole field at the semiconductor-metal interface is the dominant mechanism in controlling interdiffusion, as opposed to the Au case, where chemical trapping of the As atoms in the interlayer is the main mechanism. ²⁰ The results of Fig. 3 are in fact consistent with the evolution of the dipole layer, that is formed at low interlayer thickness and is largely unaffected by further increase in interlayer thickness. ¹⁰

CONCLUSIONS

Local studies of interface evolution with nondestructive synchrotron radiation probes show

that the local morphology of the semiconductormetal interface is of paramount importance in
determining the behavior of metallization patterns as far as exposure to oxidizing atmospheres
(corrosion) and interdiffusion are concerned.
These properties can be modulated and controlled
by interposing suitable interlayers between the
semiconductor and the metal overlayer. Possible
applications include the formation of passivating
silicon oxide layers on top of transition metal
or silicide metallizations, the use of ultrathin
catalyst layers to promote semiconductor oxidation at low temperature and pressure, the use of
diffusion barriers to control electromigration.

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